



Preparation and comparative investigation of structural and optical properties of CdS nanoparticles in PVA using chemical precipitation technique

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Abstract

The Cadmium Sulfide (CdS) nanoparticles embedded in poly vinyl alcohol (PVA) were prepared using chemical precipitation method. The prepared samples were characterized by X-ray diffraction (XRD), Scanning electron microscope (SEM), Transmission electron microscopy (TEM), UV-Vis spectrophotometer (UV-Vis), Photoluminescence (PL) spectra and Fourier transform infrared spectrophotometer (FTIR). The XRD result reveals the hexagonal structure of nanoparticles with a different grain size. The effect of quantum confinement and the shifts in optical band gap have been calculated from the PL spectra and UV-Vis spectra. The shifts in optical band gap and the particle sizes were calculated. FTIR analysis absolutely showed the formation of CdS and polymer matrix grown CdS/PVA. The CdS/PVA nanoparticle becomes located to be extra appropriate to window layer in solar cell application.

Keywords: Band gap, Cadmium Sulfide, PVA, Optical properties, Solar cell

1. Introduction

The use of semiconductors has attracted much interest in an expanding the variety of applications in various electronic, optoelectronics, sensors and energy converters. Among the II-IV group semiconductor thin films have attracted considerable attention from the research people, because their wide range of application in the fabrication of solar cells, sensors and other optoelectronic devices. Semiconductor nanocrystals are the wonderful diversions for each essential research study and the growth industrial development. This is due to their particular size-based optical and electronic properties and their exciting usage in the fields of light-emitting diode [1], electrochemical cells [2], laser [3], hydrogen producing catalyst and organic label [4]. Metal

chalcogenides like sulfides, tellurides and selenides are of the greatest significance for researchers due to the fact they may be candidate ability for the energy conversion and optoelectronics applications.

In the present years, the synthesis and characterization of group II-VI materials of cadmium sulphide (CdS) nanoparticles are attracted attention not only because of their tunable optical and electrical properties, but also due to their tuning the bandgap nature they have a variety of potential applications. CdS nanoparticles are one of the most promising materials due to its photoconducting nature and suitable band gap, $E_g = 2.42$ eV (515 nm) [5].

Among these, CdS has been studied due to inherent potential for many technological applications such as solar cells, photovoltaic, light

emitting diodes, photocatalysis, photoluminescence, infrared photo detector, environmental sensors and organic sensors [6-12]. Cadmium sulfide has two crystal forms; the more solid hexagonal wurtzite structure (observed in the mineral Greenockite) and the cubic zinc blende shape (found in the mineral Hawleyite). Nanocrystalline CdS thin films belonging to the cadmium chalcogenide family of relatives and used as window material for CdS/CdTe solar cells [13-17]. Previously, there are many reviews about cadmium sulfide nanoparticles, received by way of distinct methods and from special cadmium source precursors [18 - 21]. CdS shall be obtained in skinny film from numerous strategies [22-24] or powder form, via hydrothermal/solvothermal strategies, thermal decomposition and so forth. [25-27].

Furthermore the physicochemical properties of the system will be under influence of the effect of interaction of nanoparticles with polymer matrix [28]. Polymer is an efficient host material as capping agent and stabilizers. Since they may be prevented agglomeration and precipitation of the particles. In addition, it is the water soluble and high-quality, extremely good residences of colloid stabilizer, mechanical strength and accurate optical behavior. CdS nanoparticles is used with polymer matrix has been suggested by diverse investigators and embedded in a thermoplastic polymeric matrix had been successfully prepared. Among this polymer, PVA is a good dielectric strength, good storage capability in annealing dependent electrical and optical properties [29-30]. For over the numerous techniques were developed to synthesize CdS with divergent morphologies and structures, including solvothermal [31], hydrothermal and photochemical [32], one pot synthesis [33] and chemical precipitation method [34].

Among them, a chemical precipitation method is a simple, clean and inexpensive method to reap and extract the CdS nanoparticles. In this method, the size has been managed via arrested precipitation method. The basic trick has been to synthesis and research the nanomaterial in situ, i.e. in the same liquid medium heading of the physical adjustments and aggregation of tiny crystallites. Thermal coagulation and Oswald ripening had been controlled via double layer repulsion of crystallites the usage of non-aqueous solvents at fall temperatures for synthesis. The synthesis involved response among constituent materials in an appropriate solvent. The dopant is added to the parent solution before precipitation reaction. Surfactant is used in order to maintain the separation between the particles formed. Thus shaped nanocrystal is separated by using the

method of centrifugation, washed and vacuum dried. The dried fabric become further subjected to UV curing for viable polymerization of surfactant capping film at the surface of the nano cluster for providing genuine quantum confinement [35-37].

The improvement of nanocrystalline substances, discovery of concept of quantum confined atom and synthesis of doped nanocrystalline materials. The investigation of boom mechanism of nanoparticles is gift big medical and practical hobby. As, nanoparticles with given size and characteristics are required in nanotechnology.

Nanoparticles increase mechanism determines distribution feature of nanoparticles on length, physical-chemical properties of nanoparticles medium and so on. Because of, regarded of growth mechanism deliver possibility manage of preparation of nanoparticles and to attain nanoparticles with given parameters (mean diameter, standard deviation, coefficient polydispersity and other) and characteristics (magnetic moment). The nanoparticles boom mechanism is sufficiently complicated system and depended from many conditions (temperature, viscosity, concentration of medium and so forth). The conditions determinant of nanoparticle growth is changed in the dependence on method for the preparation of nanoparticles. The material scientists and engineers have made size able developments inside the improvement of strategies of synthesis of nanomaterials [38-40].

In this present work, we report the synthesis of CdS and CdS/PVA nanoparticles are prepared chemical precipitation method. The effect of the polymer matrix of CdS/PVA at the surface morphology, crystalline structure and optical properties are better with CdS nanoparticles. The structural, morphological and optical properties were investigated by way of XRD, SEM, TEM, and UV-Vis and photoluminescence spectroscopy. The photovoltaic parameters of the cells have been as compared. Finally the better effects have to be observed from CdS/PVA nanoparticles, so this is which may be suitable for window layer in solar cell application.

2. Materials and Methods.

Cadmium acetate [$\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$], as Cd^{2+} ion source, Thiourea [$\text{CS}(\text{NH}_2)_2$] as S^{2-} ion source and the polyvinyl alcohol (PVA) having purity (>99.9%) all reagents have been of analytical grade and used without in addition purification, which purchased from Merk India. The deionized water becomes used to prepare all the solutions in the course of the experiments.

2.1. Preparation of CdS nanoparticles in PVA

CdS/PVA nanoparticles have been prepared with the aid of chemical precipitation approach. Initially, 0.6 M of cadmium acetate mixed with 25 ml of deionized water and stirring for 1h at 40°C. Then, 1 M of thiourea merged with 25 ml of deionized water and stirring for 1h at 40°C. Then thiourea was combined with cadmium acetate drop by using drop and the reactants had been stirred continuously for other 1hr at 40°C. The pigment modified to yellow color, this is indicating formation of CdS. The 5 g of PVA is combined with 100 ml of deionized water and stirred for 24 h. Then 50 ml of polymer solution (PVA) is mixed with prepared precursor material of CdS added drop wise, after which stirred with 50°C at 24 h in 400 rpm. Then, the prepared lubricant became dried in hot air oven at 60°C for 10 h. Similarly, the CdS nanoparticles turned into prepared without PVA with the identical synthesis method.

2.2. Characterization

The crystalline structures had been analyzed using Rigaku X-ray diffractometer (MiniFlex-New 6th generation general purpose bench top XRD system for phase i.d and phase quantification). The optical studies and absorption spectra were recorded using a UV- visible spectrophotometer (Cary 8454; Agilent ,Singapore) operated inside the UV to near- IR (180-800) special region. Photoluminescence (PL) spectra are analyzed by way of Cary eclipse, Agilent technologies, Singapore. The morphology, microstructure and elemental composition of all of the samples have been analyzed the use of a scanning electron microscope (SEM). The high resolution transmission electron microscopy images were taken by a TECNAI-30 model instrument. The FTIR spectra had been obtained by Agilent technologies, Singapore, Cary 630 FTIR Sp-ectrometer, in the wavelength range of 4000 to 400 cm⁻¹.

3. Results and discussions

3.1. X-ray diffraction studies

Fig.1 indicates the X-ray diffraction spectra of CdS and CdS/PVA nanoparticles prepared at the room temperature. All the diffraction peaks have been found to correspond to the wurtzite structure of CdS hexagonal phase [JCPDS-file No: 41-1049]. In Fig.1 (a) and (b) each sample are commonly peak is (002) and (110) and adding PVA cause CdS/PVA. The XRD spectra shows extra peak detected at $2\theta = 24.50^\circ, 28.69^\circ, 36.95^\circ, 47.50^\circ$ and 50.57° which may be ascribed because of (100), (101), (102), (103) and (200) reflection planes are conformed to the

CdS/PVA pattern are hexagonal CdS shape. The broadened peaks are indicating that the sizes of particle are in nano range. The XRD diffraction peaks of CdS pattern were detected at $26.66^\circ, 43.81^\circ$ and 52.31° , which can be ascribed because of (002), (110) and (201) mirrored image planes of the hexagonal CdS structure, respectively [41-43]. The broadened the nanocrystalline CdS (002) reflection plane around $2\theta = 26.66^\circ$ this can be accredited as the reduction of intermolecular the collaboration between PVA [43].

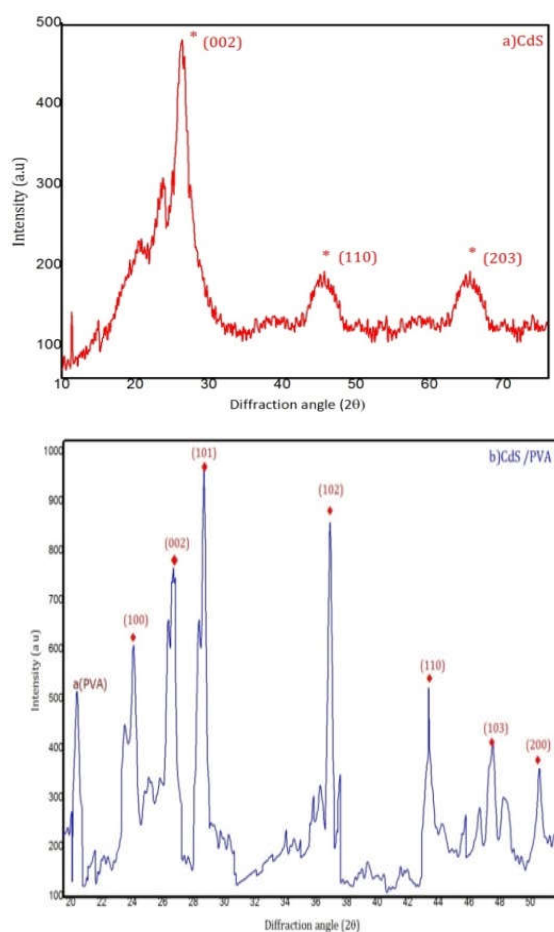


Fig.1. XRD pattern of CdS and CdS/PVA nanoparticles

Fig.1 (b) Showed that the characteristic peak at $2\theta = 20.32^\circ$, which agreed with the sample of the hydrate polymorph of PVA [44-45]. The average crystalline length of the grains has been received from X-ray diffraction pattern through the use of the scherrer's formula

$$D = K\lambda/\beta\cos\theta$$

Where, D is the grain size, K is constant to 0.94 β is the full width at half maximum (FWHM) and λ is the wavelength of the X-rays. The grain size

acquired from both samples was around 29 nm. The XRD elucidates that the film synthesized CdS/PVA are within the identity of excellent crystallinity in nature.

3.2. SEM analysis

The SEM images of CdS and CdS/PVA nanoparticles are shown in Fig. 2. It is observed that that the CdS nanoparticles in both samples are uniformly distributed. The surface morphology indicates that the CdS/PVA pattern shows the uniform distribution of CdS nanoparticles in PVA, homogeneous and small crystalline nature of CdS nanoparticles. The average particle size of CdS/PVA is determined to be 18 nm.

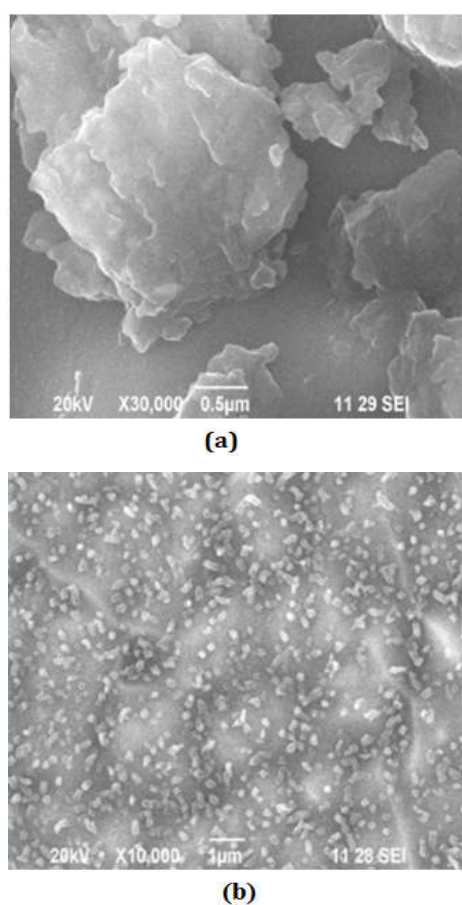


Fig.2. SEM images of (a) CdS and (b) CdS/PVA

3.3. UV-Vis optical absorption studies

The absorbance range is acquired blue shifted with admire to bulk CdS nanostructure (512 nm), and other prepared samples are compared to bulk CdS. This is indicating a quantum confinement impact [43]. Fig. 3 shows the UV-Vis absorption spectra of the CdS nanoparticles wavelength range is 503 nm and CdS/PVA nanocrystalline measured the wavelength range are 481 nm. In this reflection the

CdS wavelength is decreased by adding the polymer material of PVA. For over the CdS/PVA sample came to be the well-known which show that better absorption wavelength are as compared with CdS [42, 43]. The absorption spectrum of CdS/PVA shows a most at (481nm) and in comparison with CdS nanoparticles (503nm), 22 nm blue shift was determined. This may be due to the formation of smaller sized nanoparticles even as PVA become brought into natural CdS. This effect due to the formation of smaller sized nanoparticles whilst PVA turned into brought into pure CdS.

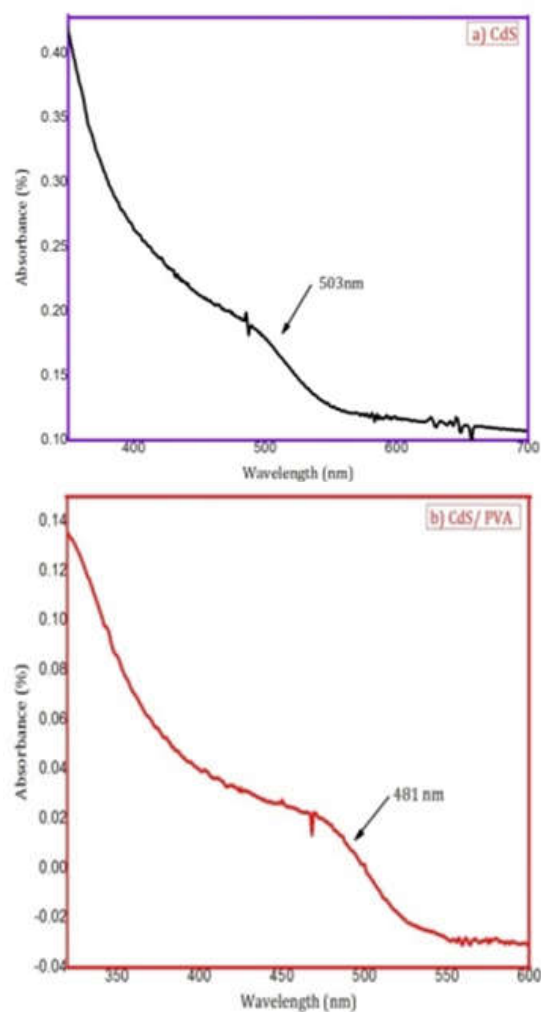


Fig.3. Optical absorption spectra of CdS and CdS/PVA

3.4. Photoluminescence studies

Fig. 4 suggests the PL spectra of CdS and CdS/PVA nanoparticles with an excitation wavelength of 490 nm. The PL spectrum of CdS exhibits a peak at 499nm (2.48 eV) whereas for CdS/PVA, the PL spectrum exhibits an emission peak around 482nm (2.57 eV) [46]. The emission band at

around 482 nm is known as blue band and an addition emission peak at 519 nm have been obtained; it is called as yellow or orange band [43].

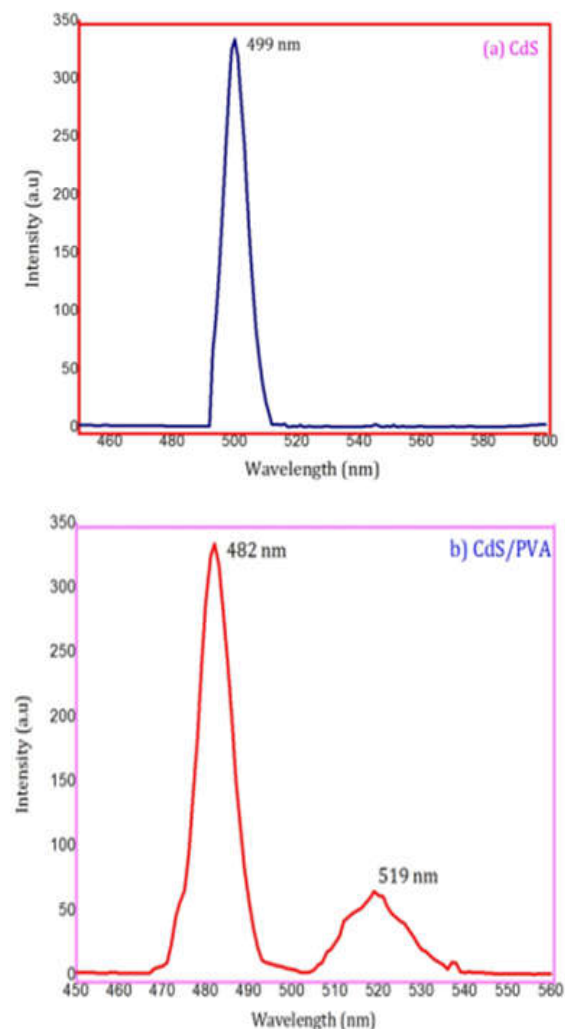


Fig.4. PL Spectra of CdS and CdS/PVA

3.5. FTIR analysis

FTIR spectra of the CdS and CdS/PVA nanoparticles are shown in Fig. 5. The diverse functional groups present within CdS and CdS/PVA nanoparticles corresponding to their wave number are given in Table 3. The peak seemed at 3414 cm^{-1} shows the presence of OH stretching. This may be due to the atmospheric moisture. The peaks at 1539 cm^{-1} and 1396 cm^{-1} are assigned to the vibrational mode of OH bending. The peak at 1228 cm^{-1} shows the presence of symmetric stretching in the molecule. The strong absorption band at 1097 cm^{-1} is assigned to the symmetric stretching (C=O bond). By comparing the IR spectrum of CdS and CdS/PVA samples, it is straight forward that each one

spectrum specially shows off identical capabilities; however the depth of intensity and the location of the peaks had been changed. It indicates that interaction within polymer chains and causes the shift in their position [47].

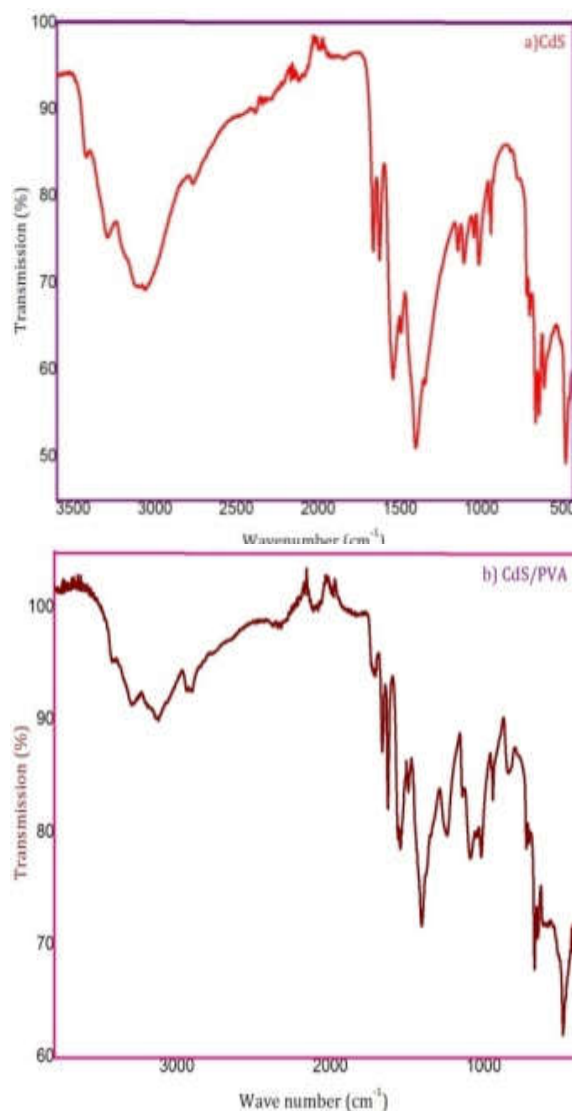


Fig.5. FTIR spectrum of CdS and CdS/PVA

3.6. TEM analysis

The pure CdS and CdS/PVA nanoparticles were morphologically investigated by means of transmission electron microscopy Fig. 6. The presented TEM images are well dispersed uniform size spherical nanoparticles can be absolutely seen within the TEM image with pretty even size distribution and no agglomeration is determined in the image. Based on acquiring the TEM picture, PVA performs a crucial role in the growth of spherical nanoparticles.

Table 1: Grain size, band gap and shift in band gap calculated from absorption spectra

Samples	Absorption edge (nm)	Bandgap from UV-Vis (eV)	Shift in band gap (eV)	Bandgap from PL spectra (eV)
CdS	503	2.46	0.06	2.48
CdS/PVA	481	2.57	0.15	2.57

Table 2: Assignment of functional groups for FTIR spectra for CdS and CdS/PVA

Wavenumber (cm ⁻¹)		Functional group
CdS	CdS/PVA	
467	473	Cd-S stretching (CdS nanoparticles)
669	660	
939	830	=CH ₂ Bending Vibrations and C-H stretching
1007	920	Out-of-plane C-H bending
1097	1090	C-O Stretching and C-O-C stretching of acetyl group present in the PVA backbone.
1149	1228	Traces of SO ₄ ⁻ ion as impurity
1396	1406	C-O-H bending
1539	1545	C=C (in ring) (2 bands)
1614	1618	C=C terminal
1659	1658	Bending (O-H)
2761	2096	C-H (aldehyde C-H)
3061	2916	C-H bonds
3294	3119	hydroxyl (-OH) groups
3414	3290	O-H Stretching and primary amide NH ₂

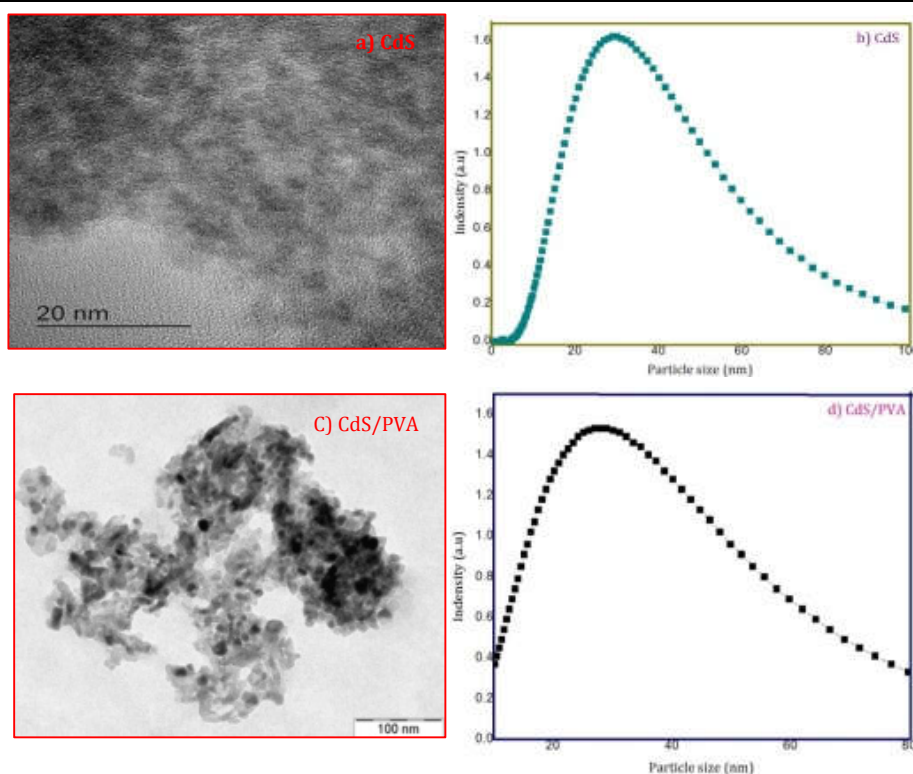


Fig.6. TEM images and particles size of CdS and CdS/PVA

The TEM micrographs Fig.6 (a) and (c) shows the particles have been more discrete, however, now not properly resolved because of the presence of the PVA. However the atoms were now not aggregated right into a large shape, even though the particles had been in contact with every other. Most of the particles have been similar in size and feature abnormal curved shapes. The common particle dimensions for all are become calculated. The element's dimensions from TEM assessment matched well with the crystallite length value calculated from XRD arrangements.

4. Conclusions

In summary, we prepared the CdS and CdS/PVA nanoparticles were synthesized using a chemical precipitation method. The XRD results secured the hexagonal phase of both samples was nanoparticles. The blue shift in the absorbance and PL spectra was attributed due to the quantum confinement effect in nanoparticles. The compared to CdS nanoparticles, the effects of CdS/PVA is showed better structural, optical and morphological belongings to study with above outcomes. The optical absorbance spectra received from the CdS/PVA nanoparticles are used for favorable optical band gaps which may be very useful for solar cellular window layer applications.

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